Synthesising Tyrian Purple

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Purple dye was at a premium in the ancient world. Clothes dyed with it carried lofty associations. Agamemnon walked on the purple cloth which his wife had laid down for him and was killed for his presumption. During Roman times the emperors wore an all-purple cloak, a symbol of imperial sovereignty, while senators and other members of the elite wore robes with purple stripes. Later, purple was used by the Christian Church and is still the official Italian name for the colour of Cardinals' robes.

Woad and Snails

There are two main natural types of purple dye. The first is indigo, which is one of the earliest used by man. A series of plants such as *Indigojera tinctoria* and *Isatis tinctoria* (woad) contain the colourless glycoside indican, which, on hydrolysis with acids or enzymes, breaks down into glucose and indoxyl. The latter is immediately converted by atmospheric oxygen into indigo (fig.1). It was by this comparatively simple method that the ancient Britons learnt to extract indigo from woad and use it as warpaint.
The second is Tyrian purple, which was derived from *Murtex* sea snails, a species which lives on sandy mudflats. One type, *Murex brandaris*, was used as a source of dye by the Phoenicians and others from the second millennium BC onwards (hence the name of the dye, from Tyre in Phoenicia); it continued to be important throughout the Greek and Roman periods. The *Murex* snail secretes a yellowish fluid, which, when boiled and treated, makes a permanent purple dye, far superior to indigo and held in high esteem for its unique, deep purple shade. Wool and cotton dyed with this so-called Royal Purple brought very high prices. The *Murex brandaris,* which was once common in the Mediterranean, is now quite rare. This is hardly surprising; one modern scholar found that 8,000 of the sea snails were needed to extract one gram of the dye.

Tyrian purple (6,6’ – dibromoindigo) has a chemical structure which is very similar to that of indigo. The only difference is that two bromine atoms have been added to the two benzene rings in the six position (fig.2).

Synthetic purple

Why did the ancients not simply add bromine to the indigo in order to create the more sumptuous Tyrian purple, rather than go through the laborious process of preparing the dye from the sea snails? In fact direct bromination of indigo itself leads successively to substitution in the 5,5' - 7,7' – 4,4' positions, which does not create the right compound. So any attempt to synthesise Tyrian purple must involve incorporation of the bromine in the appropriate position of a suitable aromatic compound prior to the final synthesis of the indigo structure.

Elucidation of the chemical structure of indigo by 19th-century chemists led to various synthetic routes to indigo being devised, which resulted in natural indigo being almost totally replaced by the synthetic material. In order to synthesise Tyrian purple it is possible to use a method based on a synthesis of indigo which was discovered in the 19th century and used commercially for a short time. This is a one-stage reaction between 2-nitrobenzaldehyde and propanone in the presence of alkali.

Tyrian purple can be synthesised from 4-bromo-2-nitrobenzaldehyde and propanone. Synthesis of 4-bromo-2-nitrobenzaldehyde is a four-stage process starting from the cheap and readily available p- toluidine. The intermediates with their yields are shown in Table 1.

Once the aldehyde is produced, it is possible to proceed in accordance with the method invented for the synthesis of indigo. Having prepared about 3g of 4-bromo-2-nitrobenzaldehyde, it is dissolved in propanone and water. Sodium hydroxide solution is then added dropwise and the mixture turns dark brown in an exothermic reaction (fig.3).

After a short time flakes of a deep purple colour separate out. These can be isolated from the orange solution by filtration and are then washed with ether. The lengthy synthesis produces about O.Sg of the gorgeously tinted dye.

Dyeing

There is still one difficulty. Both indigo and Tyrian purple are insoluble in water, so the process of vat-dyeing has to be employed. This involves reduction of the indigo compound to its soluble, so-called 'leuco-base' (cream-coloured in solution, hence its name) with alkaline sodium dithionite. The fabric to be dyed is boiled in the solution of the leuco- base and, on removal, atmospheric oxidation restores the beautiful colour of the indigo compound in the fabric. The dye is now fast. Given the complexity of this lengthy chemical process it is hardly surprising that the ancients were unable to synthesise Tyrian purple. If they wanted a dye of that very special colour they had to grub around on seashore mudflats for basketful after basketful of a certain inoffensive little sea snail.

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